HIGH PRODUCTION VOLUME (HPV)

CHEMICAL CHALLENGE PROGRAM

TEST PLAN

For The

CRUDE BUTADIENE C4 Category

Prepared by:

CMA Olefins Panel, HPV Implementation Task Group

May 1, 2000

PLAIN ENGLISH SUMMARY

This test plan addresses crude butadiene streams, which typically contain 10 to 92 percent 1,3-butadiene. Three substances will be evaluated: pure butadiene (already tested), a mid-range stream containing approximately 45-67 percent butadiene (also already tested), and a low concentration stream with approximately 10 percent butadiene (testing will be conducted). Based on existing data, the test sponsors believe the biological activity of each stream will be determined by the 1,3-butadiene content in the stream. These streams also contain other C4 substances. Additional data will be collected on these other substances, either under other test plans under the HPV Challenge Program, or through the OECD SIDS or ICCA program. The additional data will assist the test sponsors in determining whether 1,3-butadiene is the most biologically active component of the crude butadiene streams.

EXECUTIVE SUMMARY

The Chemical Manufacturers Association (CMA) Olefins Panel and its member companies hereby submit for review and public comment the test plan for the Crude Butadiene C4 category under the Environmental Protection Agency's (EPA) High Production Volume (HPV) Chemical Challenge Program (Program). It is the intent of the CMA Olefins Panel and its member companies to use new information in conjunction with a variety of existing data and scientific judgment/analyses to adequately characterize the SIDS (Screening Information Data Set) human health, environmental fate and effects, and physicochemical endpoints for this category.

This test plan addresses crude butadiene streams. Streams are mixtures of chemicals. In the case of crude butadiene streams, they are mixtures of butadiene and other chemicals, primarily chemicals containing 4 carbons. The major difference between the different crude butadiene streams is the amount of the various chemicals in the streams. Because butadiene is believed to be the most toxic chemical in the mixture, the strategy is to evaluate streams containing different concentrations of butadiene, covering the range of butadiene concentration found in these streams.

Crude butadiene streams typically contain 10 to 92 percent 1,3-butadiene, with the balance consisting predominantly of other C4 substances including 1-butene, 2-butene, isobutylene, butane and isobutane. The plan advocates addressing the category by evaluating three substances: pure butadiene (data already available), a mid-range stream containing approximately 45-67 percent butadiene (data already available), and a low concentration stream with approximately 10 percent butadiene (testing will be conducted). 1,3-Butadiene has been extensively studied and is in the SIDS process. The SIDS review is expected to be completed by the end of 2000. The test plan is based on the expectation that the presence of butadiene in the crude butadiene C4 streams will be responsible for the biological activity of the streams. This assumption is based in part on 1,3-butadiene data, and also on what is known about the other C4 compounds. Additional data will be collected on other C4 compounds as part of other test plans under the HPV Challenge Program, the ICCA program, or from chemicals already sponsored in the OECD SIDS program. The additional data will assist the Panel in determining whether butadiene is the most biologically active component of the Crude Butadiene C4 streams.

One crude butadiene stream is the full range butadiene concentrate. This stream is a mixture of butadiene, other chemicals containing 4 carbons, and other chemicals with fewer than or more than 4 carbons. Benzene is a significant component of the full range butadiene concentrate. The complete characterization of the full range butadiene concentrate stream will be accomplished by use of data from this test plan along with data from other Olefins

Panel categories (including a category with streams containing benzene) and from the data on benzene itself, which is in the SIDS process.

Predictive computer models will be used to develop much of the aquatic toxicity, environmental fate, and physicochemical data for substances in the Crude Butadiene C4 category. Aquatic toxicity testing procedures were not designed for gaseous substances like those in this category and testing will not be conducted. However, relevant information will be provided in a technical discussion that addresses the physical nature of these substances and includes a discussion of calculated aquatic toxicity data. The calculated data will be developed from a computer model used by the EPA. Relevant environmental fate information will be summarized either through the use of computer models when meaningful data can be developed or in technical discussions when computer modeling is not applicable. Physicochemical properties will be represented as a range of values according to component composition. These data will be calculated using a computer model cited in an EPA guidance document prepared for the HPV Challenge Program.

LIST OF MEMBER COMPANIES

THE OLEFINS PANEL

The Chemical Manufacturers Association (CMA) Olefins Panel includes the following member companies:

BP Amoco, p.l.c.
Chevron Chemical Company LLC
CONDEA Vista Company
The Dow Chemical Company
E. I. du Pont de Nemours and Company
Eastman Chemical Company
Equistar Chemicals, LP
ExxonMobil Chemical Company
Fina Oil and Chemical Company*
Formosa Plastics Corporation, U.S.A.
The B.F.Goodrich Company*
The Goodyear Tire & Rubber Company
Huntsman Corporation
Koch Industries*
NOVA Chemicals Inc.
Phillips Chemical Company
Shell Chemical Company
Sunoco, Inc.*
Texas Petrochemicals Corporation
Union Carbide Corporation
Westlake Chemical Corporation
Williams Olefins, LLC

* These companies are part of the Olefins Panel but do not produce CAS numbers in the Crude Butadiene C4 Category.

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TEST PLAN FOR THE CRUDE BUTADIENE C4 CATEGORY

I. INTRODUCTION

The Chemical Manufacturers Association (CMA) Olefins Panel (Panel) and its member companies have committed voluntarily to develop screening level human health effects, environmental effects and fate, and physicochemical test data for the Crude Butadiene C4 category under the Environmental Protection Agency's (EPA's) High Production Volume (HPV) Challenge Program (Program).

This plan identifies CAS numbers used to describe process streams in the category, identifies existing data of adequate quality for substances included in the category, and outlines testing planned to develop screening level data for this category under the Program. This document also provides the testing rationale for the Crude Butadiene C4 category. The objective of this effort is to identify and develop sufficient test data and/or other information to adequately characterize the human health and environmental fate for the category in compliance with the EPA HPV Program. Physicochemical data that are requested in this program will be calculated as described in EPA guidance documents.

II. DESCRIPTION OF THE CRUDE BUTADIENE C4 CATEGORY

A. The Category

The Crude Butadiene C4 Category was developed by grouping process streams that the Panel believes are similar from both a process and toxicology perspective. Twelve CAS numbers (Table 1) are used to describe these process streams. A process stream is a mixture of chemicals that arises from a chemical reaction or separation activity. Those mixtures containing 10 to 92% butadiene are referred to as "crude butadiene." With the exception of CAS 106-99-0 (which is pure 1,3-butadiene), the CAS numbers or streams in this category consist of complex mixtures of hydrocarbons. Most of the commercial products in this category have a carbon number distribution predominantly between C3 and C5. All these streams contain significant levels of 1,3-butadiene and olefins, which is why this group is considered a category for purposes of the HPV Program, and designated Crude Butadiene C4. The definitions found in the TSCA Chemical Substance Inventory for the CAS numbers included in this group are vague with respect to composition. Therefore, it is not uncommon to find that the same CAS number is correctly used to describe different streams (compositions) or that two or more different CAS numbers are used to describe the same stream (composition or process).

The crude butadiene streams arise from production processes associated with ethylene manufacturing. A description of the ethylene and associated processes is included in Appendix I. Briefly, the three process streams (sometimes referred to as products) are:

(1) Butadiene concentrate arises from the distillation of cracked gas. This typically contains 40% to about 60% 1,3-butadiene (table 2), but could contain between 10% and 80% butadiene. Other chemicals in this mixed stream are predominately chemicals containing 4 carbons.

(2) High butadiene heavy ends from the butadiene plant that arise from extractive distillation. The 1,3-butadiene content of this mixed stream ranges from 13% to 92% (table 2). Other chemicals in this mixed stream are predominately chemicals containing 4 carbons.

(3) Full-range butadiene concentrate which is the mixed stream remaining after the removal of ethylene. The 1,3-butadiene content of full range butadiene concentrate has been reported to range from 12% to 42% (table 2). Other chemicals in this mixed stream are those containing three to twelve carbons.

Note that any of the CAS numbers in this category (except the CAS number for 1,3-butadiene itself) can be used correctly to describe any of the mixed streams discussed above.

III. TEST PLAN RATIONALE

A. Overview

1. Butadiene Concentrate and Heavy Ends

Much of existing data for the Crude Butadiene C4 category are for 1,3-butadiene (Table 3), the hydrocarbon substance which is likely the most biologically active of the substances in the category and thus the major contributor to toxicological activity. 1,3-Butadiene itself is in the SIDS process and the review is expected to be completed by the end of 2000. Because of the SIDS review, butadiene has, or should have in the future, existing data of adequate quality for each of the end points. A possible exception is the acute inhalation toxicity study. The acute toxicity study included in the robust summaries, which are submitted as a separate document, contained insufficient experimental detail to assess quality. However, 1,3-butadiene has been extensively studied and acute toxicity is clearly not an issue. Our understanding of the toxicity of 1,3-butadiene would not be improved by repeating the acute toxicity study. Therefore, it was decided that the existing study was sufficient to address the acute toxicity endpoint for 1,3-butadiene. There are also data available for two crude butadiene streams. The compositions of the two previously tested crude butadiene streams were: (1) 45% 1,3-butadiene, 20% butanes, and 30% butenes and (2) 67% 1,3-butadiene, 30% butenes, and 2% 1,2-butadiene. 1,3-Butadiene is present in all the CAS numbers in this category. The presence of this chemical at concentrations >10% by weight creates a presumption under the Program that the substance would result in positive genotoxicity as the most sensitive endpoint. Supporting this presumption, the crude butadiene feedstock containing 45% butadiene has

been shown to be genotoxic.

To verify the relevance of the extrapolation of 1,3-butadiene data to substances with lower 1,3-butadiene concentrations, a full SIDS human health test battery will be conducted for a process stream containing approximately 10% 1,3-butadiene. This process stream will also include other chemicals that are included in the other streams that make up this category. The exact composition of the stream to be tested will be determined analytically at the time of testing.

The data for 1,3-butadiene together with the data from the low (approximately 10%) 1,3-butadiene-containing process stream and the data from the mid-level (45-67%)1,3-butadiene streams will be sufficient to adequately characterize the range of substances included in the category and the associated potential human health effects under the HPV Program. Crude butadiene (full range) also contains benzene. It is anticipated that similar cytogenic effects (micronuclei induction, etc.) will result from benzene, based on knowledge of the existing SIDS data set for benzene. However, it is proposed to complete a full HPV SIDS test battery for a benzene-containing stream in the High Benzene Naphtha category (volunteered for testing in 2001). The information obtained from testing a High Benzene Naphtha stream will be used in conjunction with the information obtained from testing the Crude Butadiene C4 stream described above to fully characterize the full range product.

Environmental fate and effects test data for the required endpoints do not exist for substances in this category (Table 3). This is not unexpected because these CAS numbers represent mixtures of gaseous substances and therefore, are not appropriate to be evaluated using existing standard testing guidelines. In addition, because these substances are gases, it is highly unlikely that they will pose a hazard to aquatic or terrestrial environments. As a result, aquatic toxicity and biodegradation testing will not be conducted based on the physical state of these substances and their physicochemical parameters (i.e., low boiling point, high volatility, and high Henry's Law constants). However, the environmental endpoints for photodegradation, hydrolysis, transport, and fugacity will be either calculated or discussed.

Structure-activity relationships (SARs) can be used to calculate transport (Koc) and fugacity, the latter of which is only calculated. Components of process streams in the category will partition primarily to the air, and because they have relatively low Kow values, their fate in air is the focus of environmental interest. In addition, these low Kow values suggest that they will not partition to suspended organic matter in air and therefore they will not precipitate to aquatic and terrestrial compartments.

In all cases, based on physicochemical characteristics, these substances will partition to the air at a rapid rate if released to the environment. As a result, the aquatic and terrestrial environments will not be the compartments of concern when evaluating the potential environmental impact of these substances. However, there are SARs that can be used to evaluate the potential toxicity of chemicals. A SAR will be used to calculate the toxicity of selected chemical components of the Crude Butadiene C4 category.

2. Full-Range Butadiene Concentrate

To completely characterize the toxicity of the full-range butadiene concentrate streams, data from the Crude Butadiene C4 category will be combined with data obtained during the assessment of other categories under the Olefins Panel's HPV program. Specifically, the data for the Crude Butadiene C4 category, the C-5 category, the High Benzene Naphtha category which contains benzene, and the C-3 streams category, which contains other 3 carbon compounds will, taken together, completely characterize the toxicity of this stream. Additionally, as noted, the available SIDS data sets on 1,3-butadiene and benzene will be used to assess two major determinants of toxicity of these streams.

B. Human Health Effects

1,3-butadiene (CAS #106-99-0) is likely the most biologically active component of the process streams in the Crude Butadiene C4 category. There are existing data for 1,3-butadiene, which is a SIDS listed material. The toxicity of other major components (primarily butanes and butenes), is known or will be known from current or planned testing to be sponsored by the Chemical Manufacturers Association and American Petroleum Institute. For more details on other test categories, see Section V - Other Relevant Data.

The toxicity of butadiene can be used to characterize the Crude Butadiene C4 streams represented by the CAS numbers in the category, because butadiene is typically present at greater than 10 percent. It is anticipated that positive genotoxicity will be the health effect endpoint most likely to show a positive response at the lowest test concentration for this category.

To confirm the relevance of the extrapolation of data from category members with high 1,3-butadiene content to process streams with a similar carbon number range but with lower butadiene content, a full test battery is recommended for a stream containing approximately 10% butadiene. The exact composition of the low 1,3-butadiene containing stream will be determined analytically at the time of testing. Health effects testing will be conducted by the inhalation route and will consist of the acute toxicity, Ames, mouse micronucleus, and combined repeat dose/reproductive effects/neurotoxicity screen. Of the SIDS endpoints, only the mouse micronucleus test is known to show a dose-related adverse response with butadiene exposure and with the exception of acute central nervous system effects, no other significant adverse effects have been identified in the SIDS testing conducted on other C4 substances. Additional data on other C4 components will become available through the SIDS, ICCA, and HPV programs to complete the data base for these compounds (see Section VI).

It is anticipated that the biological spectrum of activity for 1,3-butadiene, with regard to positive genotoxicity, may be reflected in the other process streams in the category. Since metabolism of butadiene is required for toxicity, and other C4 alkenes are metabolized through a common metabolic pathway, it is anticipated that mixed components will compete

for the same active enzyme sites. Different individual toxicities, which are dependent on the formation of biologically active metabolites, may be reduced, as less metabolite(s) will be produced through competition for these sites. Hence the positive genotoxicity of butadiene may in fact be reduced or eliminated by the greater presence of the other components. This is supported by existing test data for a feedstock stream containing 45% butadiene which appears to be less genotoxic than 1,3-butadiene per se. This will be further assessed by testing a stream containing a low concentration (approximately 10%) of 1,3-butadiene.

This recommended testing, in conjunction with existing data and data under development for selected components of the process streams covered by this category, will provide adequate data to characterize the Crude Butadiene C4 category for human health effects endpoints under the Program.

C. Ecotoxicity

There are three aquatic toxicity endpoints in the HPV Program:

- Acute Toxicity to Fish
- Acute Toxicity to Aquatic Invertebrates
- Toxicity to Algae (Growth Inhibition)

EPA identifies the following test methods to determine these endpoints: OECD Guideline 203, *Fish Acute Toxicity Test*; Guideline 202, *Daphnia sp., Acute Immobilization Test*; and Guideline 201, *Alga Growth Inhibition Test* [2].

The OECD aquatic toxicity test methods were not designed to assess the acute toxicity of gaseous substances like those in the Crude Butadiene C4 category. Therefore, the Panel will develop a Robust Summary Statement that addresses the physical nature of these substances and the fact that their primary route of loss will be to the air. This discussion will include calculated toxicity data for selected chemical components. The calculated data will be developed using ECOSAR, a SAR program found in EPIWIN [1].

D. Environmental Fate

Predictive models will be used to develop meaningful data for chemicals that are gaseous at relevant environmental temperatures and pressures. The environmental fate data include:

- Photodegradation
- Stability in Water (Hydrolysis)
- Transport and Distribution (Fugacity)
- Biodegradation

1. Photodegradation

Direct photochemical degradation occurs through the absorbance of solar radiation by a chemical substance. If the absorbed energy is high enough then the resultant excited state of the chemical may undergo a transformation. Simple chemical structures can be examined to determine whether a chemical has the potential for direct photolysis in water. First order reaction rates can be calculated for some chemicals that have a potential for direct photolysis using the procedures of Zepp and Cline [2].

Photodegradation can be measured [3] (EPA identifies OECD test guideline 113 as a test method) or estimated using models accepted by the EPA [4]. An estimation method accepted by the EPA includes the calculation of atmospheric oxidation potential (AOP). Atmospheric oxidation as a result of hydroxyl radical attack is not direct photochemical degradation, but rather indirect degradation. AOPs can be calculated using a computer model. Chemicals that are gases will be available for atmospheric oxidation reactions with photochemically generated hydroxyl radicals. This will be the most significant route of degradation in the environment for category members.

The computer program AOPWIN (atmospheric oxidation program for Microsoft Windows) [1] is used by OPPTS. This program calculates a chemical half-life based on an overall OH reaction rate constant, a 12-hr day, and a given OH concentration. This calculation will be performed for representative chemical components identified in the Crude Butadiene C4 category.

2. Stability in Water (Hydrolysis Testing and Modeling)

Hydrolysis of an organic chemical is the transformation process in which a water molecule or hydroxide ion reacts to form a new carbon-oxygen bond. Chemicals that have a potential to hydrolyze include alkyl halides, amides, carbamates, carboxylic acid esters and lactones, epoxides, phosphate esters, and sulfonic acid esters [5]. Stability in water can be measured [3] (EPA identifies OECD test guideline 111 as a test method) or estimated using models accepted by the EPA [4]. An estimation method accepted by the EPA includes a model that can calculate hydrolysis rate constants for esters, carbamates, epoxides, halomethanes, and selected alkylhalides. The computer program HYDROWIN (aqueous hydrolysis rate program for Microsoft windows) [1] is used by OPPTS.

It will not be necessary to run the model for the components of the streams in this category because the model cannot estimate their hydrolysis rate. Instead, a technical discussion as to why these chemicals would not be subject to hydrolysis will be prepared.

3. Chemical Transport and Distribution In The Environment (Fugacity Modeling)

Fugacity based multimedia modeling can provide basic information on the relative distribution of chemicals between selected environmental compartments (i.e., air, soil, sediment, suspended sediment, water, biota). The US EPA has acknowledged that computer modeling techniques are an appropriate approach to estimating chemical partitioning (fugacity is a

calculated endpoint and is not measured). A widely used fugacity model is the EQC (Equilibrium Criterion) model [6]. EPA cites the use of this model in its document titled *Determining the Adequacy of Existing Data* [3], which was prepared as guidance for the HPV Program.

In its document, EPA states that it accepts Level I fugacity data as an estimate of chemical distribution values. The input data required to run a Level I model include basic physicochemical parameters; distribution is calculated as percent partitioned to 6 compartments within a unit world. Level I data are basic partitioning data that allow for comparisons between chemicals and indicate the compartment(s) to which a chemical is likely to partition.

The EQC Level I is a steady state, equilibrium model that utilizes the input of basic chemical properties including molecular weight, vapor pressure, and water solubility to calculate distribution within a standardized regional environment. This model will be used to calculate distribution values for representative chemical components identified in streams in this category. A computer model, EPIWIN - version 3.02 [1], will be used to calculate the properties needed to run the Level I EQC model.

4. Biodegradation Testing

Biodegradation is the utilization of a chemical by microorganisms as a source of energy and carbon. The parent chemical is broken down to simpler, smaller chemicals, which are ultimately converted to an inorganic form such as carbon dioxide, nitrate, sulfate, and water. Assessing the biodegradability of organic chemicals using a standard testing guideline can provide useful information for evaluating chemical hazard.

Substances in this category are gaseous at room temperature. Standard OECD biodegradation test methods were not designed to assess the relative biodegradability of gaseous materials. To provide relevant information for this endpoint, a discussion will be developed on the physical nature of these substances and the fact that their primary route of loss will be to the air compartment where they will degrade through hydroxyl radical attack, which is briefly described under *photodegradation* above.

E. Physicochemical Properties

The physicochemical properties include:

- Melting Point
- Boiling Point
- Vapor Pressure
- Octanol/Water Partition Coefficient
- Water Solubility

Because the HPV substances covered under the Olefins Crude Butadiene C4 category testing plan are variable mixtures, it is not possible to develop or calculate a single numerical value for some of the physicochemical properties. For example, a product that is a mixture of chemicals does not have a melting point, but rather a melting range. Values for physicochemical properties will be represented as a range of values according to the product's component composition and based on the results of computer modeling.

Data for the physicochemical endpoints will be developed using sources recommended by EPA. There are estimation models (Structure-Activity Relationships, SAR) for each of these endpoints in the EPIWIN [1] (Estimation Program Interface for Windows) computer program and EPA has indicated that it will accept estimated data using this program [4].

Boiling point, melting point, and vapor pressure ranges will be determined using the MPBPVP subroutine in EPIWIN. K_{ow} and water solubility will be calculated using KOWIN and WSKOW subroutines, respectively. There is more information on calculating data for the HPV chemical program in the EPA document titled, *The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program.*

IV. TEST PLAN SUMMARY

The following testing, modeling, and technical discussions will be developed for the Crude Butadiene C4 category (Table 3):

- Conduct one test battery for all SIDS human health endpoints on a product (stream) containing approximately 10% 1,3-butadiene (exact composition to be determined at the time of testing).
- Compare evaluated endpoints to those for 1,3-butadiene and the other identified data and prepare a technical discussion in terms of their representation of potential human health effects for this category.
- Prepare a technical discussion of the potential aquatic toxicity of selected chemical components comprising streams in this category using modeled data.
- Prepare a technical discussion on the potential of chemical components comprising streams in this category to photodegrade.
- Prepare a technical discussion on the potential of chemical components comprising streams in this category to hydrolyze.
- Prepare a technical discussion on the potential biodegradation of chemical components of streams in this category.
- Calculate fugacity data for selected chemical components of streams in this category.
- Calculate physicochemical data as described in the EPA document titled, *The Use of Structure-Activity Relationships (SAR) in the High Production Volume Chemicals Challenge Program.*

Summaries of results will be developed once the data and analyses are available. This test plan is expected to provide adequate data to characterize the human health effects and environmental fate and effects endpoints for the category under the Program.

V. OTHER RELEVANT DATA

The Crude Butadiene C4 test category addresses crude butadiene streams, which typically contain 10 to 92 percent 1,3-butadiene, with the balance consisting predominantly of other C4 substances including 1-butene, 2-butene, isobutylene, butane and isobutane. The plan proposes addressing the category using data for three substances: pure butadiene, a mid-range stream containing approximately 45-60 percent butadiene, and a low concentration stream with approximately 10 percent butadiene. The test plan is based on the expectation that the biological activity of 1,3-butadiene will be responsible for the effects seen in the testing of the crude butadiene streams. This assumption is based in part on 1,3-butadiene data, and also what is known about the other C4 compounds. Additional data will be collected on other components of these streams as part of other test plans under the HPV Challenge Program, the ICCA program, or from chemicals already sponsored in the OECD SIDS program.

Propane and propylene account for most of the C3 materials found in the crude butadiene streams. The Petroleum HPV Test Group, managed by API, has taken responsibility for propane under the HPV program. The data set for propylene is expected to be covered under the ICCA program.

Major C4 components other than 1,3-butadiene, commonly present in crude butadiene streams included butane, isobutane, 1-butene, isobutylene and 2-butene. The Petroleum HPV Test Group has taken responsibility for butane and isobutane. The CMA Olefins Panel will complete the data set for 1-butene as part of a separate test category (Category 2 Low butadiene C4). Isobutylene and 2-butene are already in the OECD SIDS program. Therefore, data already exists or will be developed for each of the major C4 components in the Crude Butadiene C4 category.

The full-range butadiene concentrate stream included in this test category consists of the entire C3+ or C4+ compounds produced in the cracking furnace. This stream is only rarely isolated and is usually site-limited. Normally this stream is further processed by distillation into a C3 fraction (propylene stream), a C4 fraction (C4 butadiene concentrate) and a C5+ fraction (pyrolysis gasoline). A separate test plan, sponsored by the CMA Olefins Panel, will be submitted for the C3 fraction. The C4 fraction is the material of primary interest in this test category. Testing of the C5+ fraction will be done under separate test categories sponsored by the CMA Olefins panel. More specifically, a separate test plan will be submitted for the C3 propylene stream, for the predominantly C5 category, for a C6+ high benzene naphtha category and for a low benzene naphtha category. For a complete list of test categories sponsored by the CMA Olefins Panel see table 4. It is also worth noting that in addition to 1,3-butadiene, many of the other major components found in the full-range butadiene

concentrate stream are in the OECD SIDS program including benzene, toluene and dicyclopentadiene. While testing a C3+ or C4+ stream is not specifically proposed, sufficient data will become available to characterize this material as a result of the testing of the various cuts previously mentioned.

REFERENCES

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2. Zepp, R. G., and D. M. Cline. 1977. Rates of Direct Photolysis in the Aqueous Environment. Environ. Sci. Technol. 11:359.366.
3. US EPA. 1999. Determining the Adequacy of Existing Data. OPPT, EPA.
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5. Neely, W. B. 1985. Hydrolysis. In: W. B. Neely and G. E. Blau, eds. Environmental Exposure from Chemicals. Vol I., pp. 157-173. CRC Press, Boca Raton, FL, USA.
6. Mackay, D., A. Di Guardo, S. Paterson, and C. E. Cowan. 1996. Evaluating the Environmental Fate of a Variety of Types of Chemicals Using the EQC Model. Environ. Toxicol. Chem. 15:1627-1637.

Table 1. CAS Numbers And Descriptions.

CAS Number	CAS Number Description
106-99-0	1,3-Butadiene
25167-67-3	Butenes
68477-41-8	Distillate (Petroleum), Extractive C3-5
68955-28-2	Gases, (Petroleum) Light Steam Cracked, Butadiene Conc.
68476-44-8	Hydrocarbons, >C3
68512-91-4	Hydrocarbons C3 – C4 rich petroleum distillates
68187-60-0	Hydrocarbons, C4, Ethane-Propane Cracked
68476-52-8	Hydrocarbons, C4, Ethylene Manufactured By-Product
68956-54-7	Hydrocarbons C4, unsaturated
69103-05-5	Hydrocarbons, C4-7, Butadiene Manufactured By-Product
64742-83-2	Naphtha, (Petroleum), Light Steam-Cracked
68513-68-8	Residues (Petroleum), Deethanizer Tower

Table 2. Typical Composition Ranges (Percent) For Crude Butadiene Streams

Component	Crude Butadiene or Butadiene Concentrate	Heavy Ends	Full-Range Butadiene Concentrate
Tert-butyl catechol	0 - 0.01		
Methanol	0.0 - 0.3		
Propylene	0.0 - 1.9		0 - 4.0
Other C3 &lighter	0.5 - 1.7		0 - 1.0
Methylacetylene & Propadiene	0.0 - 2.3		
Ethyl & Vinylacetylene	0.7 - 3.0		
Isobutane	0.4 - 22		0.0 - 1.1
n-Butane	1.5 - 30	0.0 - 6.0	1.0 - 4.5
Isobutylene	0.5 - 29		5.0 - 12
cis & trans-butene-2	3.5 - 54	5 - 50	1.5 - 6.4
Butene-1	2.5 - 25	0.0 - 4.0	5.0 - 11
1,3-Butadiene	**10 - 82**	**13 - 92**	**12 - 42**
1,2-Butadiene	0.0 - 1.4	0.0 - 2.0	0.0 - 1.0
C5 & Higher	0.0 - 8.0		
Vinylcyclohexene	0.0 - 1.0		
Isopentane		0.0 - 3.0	
C8		0.0 - 4.0	
1,4-pentadiene			0.2 - 1.2
Pentene-1			0.5 - 2.3
Isoprene			0.6 - 3.2
cis & trans-pentene-2			0.1 - 2.0
1,3-cyclopentadiene			1.0 - 9.5
cis & trans-1,3-pentadiene			1.0 - 7.2
cyclopentene			0.5 - 2.6
cyclopentane			2.0 - 4.0
C6-C8 non-aromatics			2.0 - 12
Benzene			11 - 42
Toluene			1.8 - 25
Xylenes			0.1 - 4.0
Ethylbenzene			0.1 - 1.3
Dicyclopentadiene			2.0 - 10
Indene			0.3 - 1.9
Naphthalene			0.2 - 1.6
Other C9 and higher			1.5 - 8.7

Note 1:The balance of these streams is expected to be other hydrocarbons that have boiling points in the range of the listed components.
Note 2: The listed highs and lows should not be considered absolute values for these limits. They are instead the highs and lows of the reported values, and are expected to be typical limit values.
Note 3: The definitions, found in the TSCA Chemical Substance Inventory, for the CAS numbers included in this group are vague with respect to composition. Therefore, it is not uncommon to find that the same CAS number is correctly used to describe different streams (compositions) or that two or more different CAS numbers are used to describe the same stream (composition).

Table 3. Assessment Plan For Crude Butadiene C4 Category Under The Program. Robust summaries for existing studies are submitted separately.

Product Description	Human Health Effects						Ecotoxicity			Environmental Fate				
	Acute Toxicity	**Genetic Point Mut.**	**Genetic Chrom.**	**Sub-chronic**	**Develop-mental**	**Reproduc-tion**	**Acute Fish**	**Acute Invert.**	**Algal Toxicity**	**Physical Chem.**	**Photo-deg.**	**Hydro-lysis**	**Fugacity**	**Biodeg.**
1,3-Butadiene	**v**	**v**	**v**	**v**	**v**	**v**[1]	NA	NA	NA	SAR	TD	TD	CM	TD
Mid-range 1,3-Butadiene- 67% 1,3-butadiene, 30% butenes, 2% 1,2-butadiene	RA	**v**	RA	RA	RA	RA	NA	NA	NA	SAR	TD	TD	CM	TD
Mid-range 1,3-Butadiene 45% 1,3-butadiene, 20% butanes, 30% butenes	**v**	**v**	**v**	**v**	RA	RA	NA	NA	NA	SAR	TD	TD	CM	TD
Low 1,3-Butadiene[2]	T	T	T	T	T	T	NA	NA	NA	SAR	TD	TD	CM	TD

v	Adequate existing data available	TD	Technical discussion proposed	SAR	Structure Activity Relationship
1	These data are not yet available, but should be addressed as part of the SIDS program	CM	Computer Modeling proposed		
		RA	Read Across		
2	The target concentration of 1,3-butadiene is 10%. Actual composition will be determined analytically and provided when testing is complete.				
NA	Test not applicable due to physical nature of category member	T	Proposed Testing		

Appendix I

ETHYLENE PROCESS DESCRIPTION

A. The Ethylene Process

1. Steam Cracking

Steam cracking is the predominant process used to produce ethylene. Various hydrocarbon feedstocks are used in the production of ethylene by steam cracking, including ethane, propane, butane, and liquid petroleum fractions such as condensate, naphtha, and gas oils. The feedstocks are normally saturated hydrocarbons but may contain minor amounts of unsaturated hydrocarbons. These feedstocks are charged to the coils of a cracking furnace. Heat is transferred through the metal walls of the coils to the feedstock from hot flue gas, which is generated by combustion of fuels in the furnace firebox. The outlet of the cracking coil is usually maintained at relatively low pressure in order to obtain good yields to the desired products. Steam is also added to the coil and serves as a diluent to improve yields and to control coke formation. This step of the ethylene process is commonly referred to as "steam cracking" or simply "cracking" and the furnaces are frequently referred to as "crackers".

Subjecting the feedstocks to high temperatures in this manner results in the partial conversion of the feedstock to olefins. In the simplest example, feedstock ethane is partially converted to ethylene and hydrogen. Similarly, propane, butane, or the hydrocarbon compounds that are associated with the liquid feedstocks are also converted to ethylene. Other valuable hydrocarbon products are also formed, including other olefins, diolefins, aromatics, paraffins, and lesser amounts of acetylenes. These other hydrocarbon products include compounds with two or more carbon atoms per molecule, i.e., C2, C3, C4, etc. Propane and propylene are examples of C3 hydrocarbons and benzene, hexene, and cyclohexane are a few examples of the C6 hydrocarbons.

2. Refinery Gas Separation

Ethylene and propylene are also produced by separation of these olefins streams, such as from the light ends product of a catalytic cracking process. This separation is similar to that used in steam crackers, and in some cases both refinery gas streams and steam cracking furnace effluents are combined and processed in a single finishing section. These refinery gas streams differ from cracked gas in that the refinery streams have a much narrower carbon number distribution, predominantly C2 and/or C3. Thus the finishing of these refinery gas streams yields primary ethylene and ethane, and/or propylene and propane.

B. Products of the Ethylene Process

The intermediate stream that exits the cracking furnaces (i.e., the furnace effluent) is

forwarded to the finishing section of the ethylene plant. The furnace effluent is commonly referred to as “cracked gas” and consists of a mixture of hydrogen, methane, and various hydrocarbon compounds with two or more carbon atoms per molecule (C2+). The relative amount of each component in the cracked gas varies depending on what feedstocks are cracked and cracking process variables. Cracked gas may also contain relatively small concentrations of organic sulfur compounds that were present as impurities in the feedstock or were added to the feedstock to control coke formation. The cracked gas stream is cooled, compressed and then separated into the individual streams of the ethylene process. These streams can be sold commercially and/or put into further steps of the process to produce additional materials. In some ethylene processes, a liquid fuel oil product is produced when the cracked gas is initially cooled. The ethylene process is a closed process and the products are contained in pressure systems. (See figure 1 for a pictorial representation of the ethylene manufacturing process.)

The final products of the ethylene process include hydrogen, methane (frequently used as fuel), and the high purity products ethylene and propylene. Other products of the ethylene process are typically mixed streams that are isolated by distillation according to boiling point ranges. It is a subset of these mixed streams that make up the constituents of the Crude Butadiene C4 category.

C. The Crude Butadiene C4 Products

1. Crude Butadiene Or Butadiene Concentrate

Butadiene concentrate is the product in the C4 Crude Butadiene Category. The concentrate is separated by distillation from the condensed portion of the cracked gas. Typically, butadiene concentrate is a fairly narrow boiling range mixture and consists predominately of C4 hydrocarbons. The butadiene concentrate may also contain lesser amounts of C3 or lighter hydrocarbons and C5 and heavier hydrocarbons, because the separation technology is not perfect. The 1,3-butadiene content of this product is typically 40% to 60%, but has been reported to range from 10% to about 80% (table 2). Crude butadiene is sometimes produced in "on purpose" butadiene units using, for example, an oxydehydrogenation process.

2. High Butadiene-Content Heavy Ends From The Butadiene Plant

Several different technologies are used to separate 1,3-butadiene from C4 butadiene concentrate produced by the ethylene process. All of these processes use a solvent for the separation.

In one technology, the C4 butadiene concentrate is fed to an extractive distillation (ED) column and a C4 mixture referred to as “raffinate” (i.e., C4 olefins and paraffins) is separated from the top of the distillate column. The bottom from the ED column consists of the solvent, rich in 1,3-butadiene, and small amounts of other C4s. The rich solvent is fed to the solvent stripper where the 1,3-butadiene and other C4s are taken overhead. The stripped, lean solvent is transferred from the bottom of the stripper back to the ED tower. The overhead of the

stripper is condensed and fed to the rerun tower (or postfractionator) where high purity 1,3-butadiene is produced as the overhead. Bottoms of the rerun tower consist of the higher boiling components of the butadiene concentrate (e.g., 1,2-butadiene). The 1,3-butadiene content of the heavy ends from the butadiene plant covered by this test plan ranges from 13% to 92% (table 2).

3. Full-Range Butadiene Concentrate

Butadiene concentrate sometimes consists of the entire C3+ or C4+ portion of the cracked gas stream (full-range butadiene concentrate). In this case, the carbon number distribution is between C3 and C12 or even higher. Normally the C4+ full-range butadiene concentrate is split by distillation into two streams, a butadiene concentrate stream, described above, and pyrolysis gasoline stream. The C3+ stream is separated into these two streams plus a C3 stream. The C3 stream and pyrolysis gasoline will be covered by separate test categories sponsored by the CMA Olefins Panel. There are only two known examples where these broad-range streams have been reported to have been isolated. In both cases, it was a result of a shutdown of process equipment. The C4+ stream was site limited and the C3+ was not. The 1,3-butadiene content of full range butadiene concentrate has been reported to range from 12% to 42% (table 2).

4. 1,3-Butadiene

High purity 1,3-butadiene (99.5%+) is produced by separation from the C4 butadiene concentrate (or crude butadiene) produced by the ethylene process. This separation is accomplished by using a solvent process, either extraction or more typically extractive distillation. “On purpose” units also produce a small percentage of the commercially available 1,3 butadiene by dehydrogenation and subsequent separation.

Figure 1. Flowsheet for Crude Butadiene C4 Test Group

Note: In addition to Crude Butadiene C4 products & streams, additional HPV products & streams associated with these units are show below for clarity.

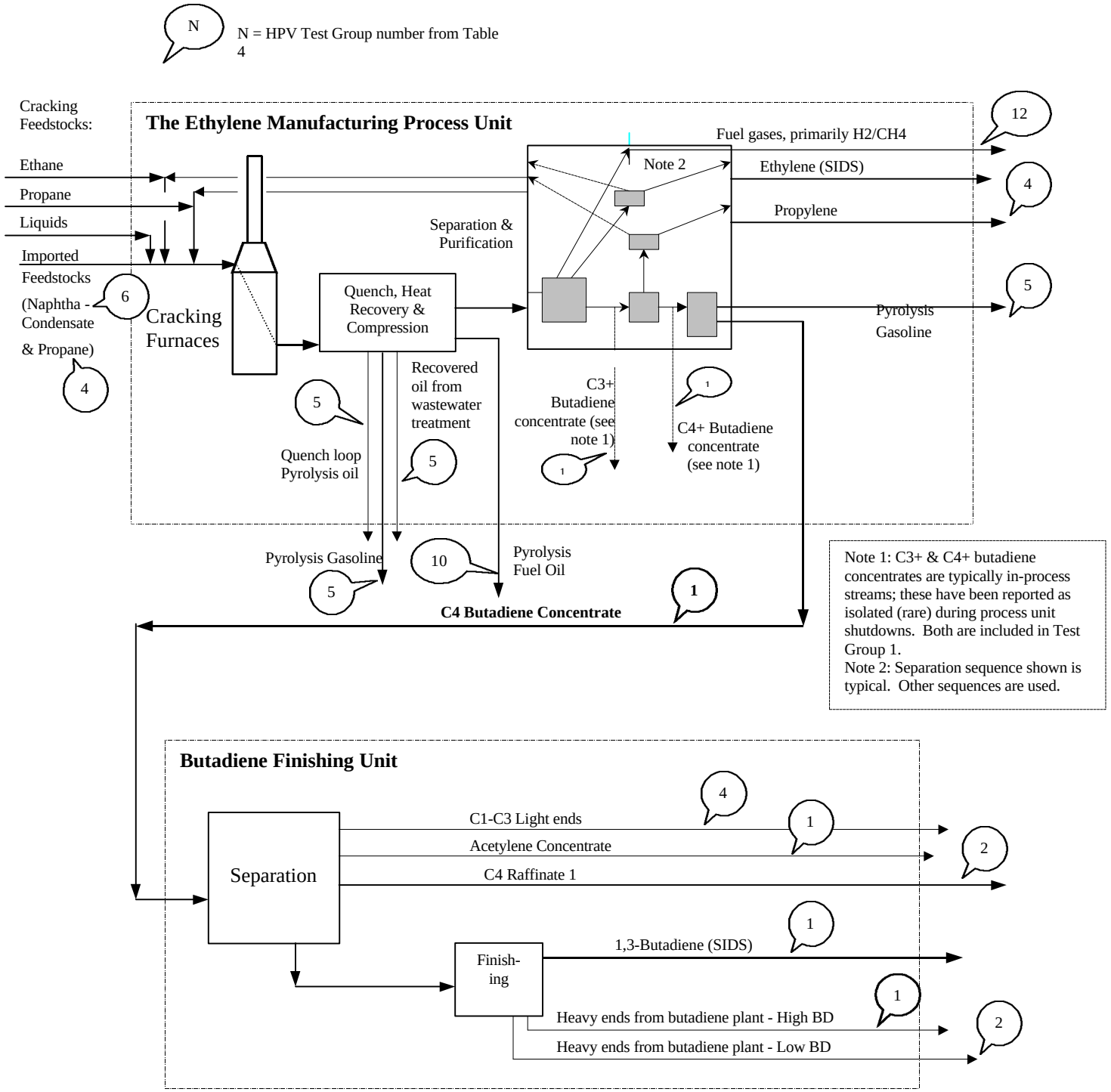

Table 4. CMA Olefins Panel Sponsored Test Categories

Category Number	Category Description
1	Crude Butadiene C4
2	Low Butadiene C4
3	C5 Non-Cyclics
4	Propylene Streams (C3)
5	High Benzene Naphthas (C6-C12, predominantly C6)
6	Low Benzene Naphthas (C7-C12)
7	Resin Oil - High Dicyclopentadiene
8	Resin Oil - Low Dicyclopentadiene
9	Resin Oil - Dicyclopentadiene Concentrate and Crude Dicyclopentadiene
10	Fuel Oils (C8+)
12	Fuel Gases